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TREATING PROCESS

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13 Claims. (Cl. 117—62)

The present invention relates to certain novel improvements in the procedures described and claimed in copending application Serial No. 738,919, filed June 2, 1958, now issued as U.S. Patent 2,870,041. This application is a continuation-in-part of said Serial No. 738,919, the disclosure of the latter being incorporated herein by reference.

According to the abovementioned Serial No. 738,919, undesirable odors, such as aldehyde and amine odors, in filamentary and sheet material treated with aldehyde resins and normally subject to such odors as a result of the aldehyde resin treatment, are effectively controlled by impregnating the material with a compound supplying the HSO_3^- ion, at any stage in the treatment of the material from application of the resin until after curing thereof, and thereafter drying the material at elevated temperature in the presence of the HSO_3^- ion, the amount of compound utilized being sufficient to react with all free and potentially free aldehyde in the material and varying between 0.01 mols and 1.0 mols, per mol of aldehyde in the resin, when the compound is applied after curing, and being at least one mol per mol of aldehyde in the resin when the compound is applied prior to curing.

The above procedures, as described and claimed in Serial No. 738,919, give satisfactory odor control whether the HSO_3^- ion is applied prior to curing of the resin or subsequent thereto. However, according to the present invention, it has been found that, with certain resin-treated materials where the HSO_3^- ion is applied after partial or full curing of the resin, the amount of HSO_3^- ion needed to obtain effective odor control may be materially reduced if the cured material is impregnated with HSO_3^- ion in the presence of a water-soluble, readily removable alkaline agent present in amount sufficient to provide a pH between 6 and 12 during impregnation. Typical of the cured resin-treated materials with respect to which the present invention is of particular importance are cotton fabrics which have previously been rendered water-repellent by conventional resin treatments, with or without the use of hydrophobic softeners; resin-treated cotton fabrics containing higher twist yarns and relative tight constructions; and resin-treated viscose or rayon fabrics. Other materials may also be treated in accordance with the invention described herein.

The modification described in the preceding paragraph makes possible complete odor control using a reduced amount of the odor control agent within the limits prescribed in Serial No. 738,919, particularly in the case of resin treated repellent and/or tightly woven cotton fabrics and rayon fabrics. Other advantages of this modified process include a reduction in the amount of any wetting agents used in the HOS_3^- ion impregnating bath; improved compatability of the HSO_3^- treatment with auxiliary agents such as filamentary surface softeners, lubricants, sewing assistants (needle friction lubricants), etc.

Without intending to limit the invention to any particular theory, it appears that the alkaline agent, under the conditions prescribed herein, promotes swelling and penetration of the cured filamentary and sheet material in aqueous media so that the HSO_3^- ion is allowed to more readily reach the site of the aldehyde resin. After performing its apparent swelling, penetrating and/or other function, the volatile alkaline agent is driven off during the drying operation.

According to the invention, any water-soluble organic or inorganic alkaline agent which does not deleteriously affect the material, is readily removable by heat during the drying operation or otherwise, e.g. by steam distillation, azeotropic distillation, evaporation or decomposition at temperatures between 80° F. and 400° F. and provides the desired pH between 6 and 12 may be used for the purposes described herein. Aqueous ammonia, i.e. ammonium hydroxide, is particularly desirable because of its availability, effectiveness and low cost. However, there may also be used other water-soluble alkaline materials, for example, mono, di, tri and tetra alkyl, aryl or substituted alkyl or aryl ammonium hydroxides, specifically mono-ethyl, diethyl, triethyl and tetraethyl ammonium hydroxide as well as other substituted or unsubstituted basic nitrogen compounds, such as morpholine, pyridine, pyrrolidine, pyrrole and diamines such as alkyl diamine, typically ethylene diamine.

Impregnation of the resin-treated material with HOS_3^- ion and alkali, according to the invention, may be carried out after either full or partial curing of the resin. Any convenient impregnating method, e.g. saturation and squeeze, spraying and/or vapor application, may be used. Typically, the fully or partially cured resin-treated material may be padded with an aqueous solution containing the desired amounts of HSO_3^- ion and alkaline agent. One suitable method involves a single pad of the material conducted at room temperature or other convenient temperature (e.g. 70° to 212° F.), followed by drying and curing. Alternatively, a multiple padding operation may be used. This may comprise one or more consecutive paddings with sodium bisulfite, or a conventional washing agent commonly used in resin after-finishing, at room temperature or other convenient temperature (70° to 212° F.), followed by one or more paddings with wash water to remove soluble materials and then further padding through a bath including the odor control agent and the volatile alkaline agent at room temperature or other convenient temperature followed by drying and curing.

As in Serial No. 738,919, any water-soluble organic and inorganic compound capable of forming HSO_3^- ions in aqueous solution may be used as the odor controlling agent of the present invention. Particularly desirable is sodium meta bisulfite ($Na_2S_2O_5$) because of its availability, and low cost. However, there may also be used other water-soluble salts of sulfurous acid, for example, the sulfites and bisulfites of the alkali metals of group IA of the periodic table, i.e. lithium, sodium, potassium, rubidium and cesium and of the alkaline earth metals of group IIA, such as beryllium, magnesium, and calcium, as well as those of zinc and aluminum. Ammonium bisulfite, sulfurous acid per se or sulfur dioxide in solution ($SO_2+H_2O \leftrightarrow H_2SO_3$) may also be used.

It is indicated as desirable in Serial No. 738,919 to apply the HSO_3^- ion to the material undergoing treatment at a pH between 4 and 8, preferably 5 and 6, for optimum odor control. These pH conditions are also observed with the improved procedure described herein. Thus, while the material is impregnated with HSO_3^- ion at a pH between 6 and 12 due to the presence of the alkaline agent, removal of the alkali during the initial stages of drying brings the pH within the range of 4

and 8. The amount and nature of the alkali, as well as the drying conditions, should therefore, be selected to provide the initial optimum impregnating pH between 6 and 12 and the subsequently desired lower pH in the range of 4 to 8. Drying and curing of the impregnated material may be carried out at temperatures of the order of 225° F. to 400° F. for a period of time varying between 20 minutes and 10 seconds.

The impregnating solution used herein may also include, in addition to the HSO_3^- ion and volatile alkaline agent, suitable wetting agents, e.g. Tergitol TMN (an alkyl ether of polyethylene glycol) or Wooncopen GW Reg. (a nonionic fatty amine complex). Other conventional finishing agents, e.g. filamentary surface softeners, lubricants and sewing assistants (needle friction assistants) may also be included in the impregnating solution.

An amount of odor control agent falling within the range specified in Serial No. 738,919, namely, 0.01 mol to 1.0 mol per mol of aldehyde in the resin, may be used for the purposes of the present invention. It will be appreciated, however, from the foregoing that the present process will give the same degree of odor control with smaller amounts of odor control agent. The optimum amount of odor control agent to be used in any case depends upon other operating factors such as the nature of the material being treated, etc.

For the purpose of determining whether the desired degree of odor control has been attained, the treated fabric may be steamed and the residual odor in the steam and hot fabric checked by smelling. Complete odor elimination is obtained when no formaldehyde or amine odor can be detected by this method.

The invention is illustrated, but not limited, by the following examples wherein parts and percentages are by weight.

Example I

An apparel type non-woven fabric produced by impregnating a fibrous nylon-viscose web with a binder mixture including a flexible film-forming acrylic polymer (namely, carboxylated acrylic emulsion), a thermosetting resin (methylated methylol melamine) and a resin catalyst (zinc nitrate); drying and curing, was subjected to an after-pad treatment to give 100% wet pickup using the following aqueous mixture:

	Parts
Sodium bisulfiite	3
Nonionic fatty amine complex wetting agent (Wooncopen GW Regular)	0.1
30% polyethylene emulsion	1

Per 100 parts aqueous mixture.

The thus treated non-woven fabric was dried and cured at 250° F. for 2 minutes to give a product which was odor free.

Two parts of 28% aqueous ammonia was added to the above bath, according to the present invention, and the process was repeated on a similar piece of fabric. It was found that equivalent odor free results were obtained using only two parts of sodium bisulfite in the bath. The ammonia, therefore, permitted a 50% reduction in the amount of odor control agent.

Example II

A 10% by weight solution of sodium bisulfite with 0.5% nonionic fatty amine complete wetting agent (i.e. Wooncopen GW Regular) and 1% polyethylene softener 30% emulsion was maintained at elevated temperature (120° F.) in a pad box. A woven rayon fabric which had previously been treated with thermosetting resin (dimethylol urea) and catalyst (1-propanol amine hydrochloride), dried and cured was padded through the pad box and squeezed to leave about 65% wet pickup of the solution, dried and cured at 250° F., for two minutes to give a fabric having improved odor control characteristics although some odor was noticeable under severe steaming.

When sufficient aqueous ammonium hydroxide was added to the bisulfite solution to raise the pH to between 7 and 8, and the process was repeated, an odor free product was obtained using only 4% bisulfite, 0.1% by weight of wetting agent, and a bath temperature of 70° F. No odor was noticeable even under severe steaming.

Example III

A 3.5% by weight solution of sodium bisulfite with 0.2% by weight of the nonionic fatty amine complex wetting agent of Example II and 1% aminoethyl ethanol stearate softener 30% emulsion was maintained at elevated temperature (180° F.) in a pad box. A woven cotton fabric which had been treated with thermosetting resin (dimethylol ethylene urea), catalyst (magnesium chloride), and polyethylene softener, dried and cured, was padded through the pad box and squeezed to leave about 65% wet pickup of the solution, dried and cured at 250° F. for 2 minutes to give improved odor control in the treated fabric. Some odor was, however, noticeable on steaming the fabric but when aqueous ammonium hydroxide was added to raise the pH of the pad solution to pH of 8 and the procedure repeated, this odor was eliminated and the resulting fabric was odor-free even on steaming.

Example IV

A 6% by weight solution of sodium bisulfite with 0.1% by weight of the nonionic fatty amine complex wetting agent used in Example II was maintained near the boil (190° F.) in a pad box. Woven cotton fabric which had previously been treated with thermosetting resin (dimethylol ethylene urea) and permanent type water repellents (stearamidomethyl pyridinium chloride or reactive silicone polymer repellent with its catalyst, zinc octoate), dried and cured, was padded and squeezed to leave about 65% wet pickup of the solution on the fabric, dried and cured at 250° F. for two minutes. The odor characteristics of the thus treated fabric were significantly improved but some odor was noticeable on steaming. However, when 3 parts of 28% aqueous ammonium hydroxide was added to the pad box and the process repeated, using a lower impregnating temperature of 100° F., the resulting product was odor-free even on steaming.

Example V

A 3% by weight solution of sodium bisulfite with 0.1% by weight of the nonionic fatty amine complex wetting agent used in Example II was maintained at room temperature (68–72° F.). A woven cotton fabric which had previously been treated with thermosetting resin (dimethylol urea) and a catalyst (1-propanol amine hydrochloride) dried and cured, was sprayed on both faces with the above mixture to leave about 30% wet pickup, dried and cured at 250° F. for two minutes. The fabric had good odor control characteristics although on steaming, some aldehyde odor was noticeable. The process was repeated after the addition of 3% by weight of 28% aqueous ammonium hydroxide to the spray mixture and the resulting product was odor-free even under severe steaming.

Example VI

A two-step process was carried out by giving the resin-treated cotton fabric of Example III a soaping-off (washing) after-treatment, followed by drying and padding as follows:

The fabric was padded and squeezed through one bath containing 0.25% sodium bisulfite with 0.1% by weight of the nonionic fatty amine complex wetting agent of Example II at 130° F., washed through three wash boxes, padded wet and dry through a bath at 130° F. to pick up by fabric weight 2% sodium bisulfite, 0.1% nonionic fatty amine complex wetting agent, 0.5% ammonium

hydroxide, 0.2% polyethylene softener, dried and cured at 250° F. for two minutes. The fabric product was odor free.

It will be appreciated that various modifications may be made in the invention described herein without deviating from the scope thereof as defined in the appended claims wherein we claim:

1. In a process for controlling the odor of a cured, aldehyde resin-treated filamentary or sheet material involving the steps of impregnating said material with a compound supplying the HSO_3^- ion subsequent to curing of said aldehyde resin followed by drying in the presence of said HSO_3^- ion, the improvement which comprises impregnating said material with the HSO_3^- ion, after application and curing of the resin, in the presence of a volatile, water-soluble alkaline agent in sufficient amount to maintain a pH of between 6 and 12 during said impregnation step whereby the effectiveness of said HSO_3^- ion in controlling odor is increased.

2. The improvement of claim 1 wherein said alkaline agent is aqueous ammonia.

3. The improvement of claim 1 wherein said alkaline agent is volatilized during drying to reduce the pH to one within the range of 4 to 8.

4. The improvement of claim 1 wherein the alkaline agent is present in amount sufficient to maintain a pH between 8 and 10 during said impregnation step.

5. The improvement of claim 1 wherein said compound is a water-soluble salt of sulfurous acid and the volatile alkaline agent is a water-soluble amine.

6. The improvement of claim 1 wherein said compound is a water-soluble salt of sulfurous acid and the volatile alkaline agent is ammonium hydroxide.

7. The improvement of claim 1 wherein said compound is sodium bisulfite and said volatile alkaline material is ammonium hydroxide.

8. The process of claim 1 wherein said material is a fibrous material.

9. The process of claim 1 wherein said material is a knitted fabric.

10. The process of claim 1 wherein said material is a non-woven fabric.

11. The improvement of claim 1 wherein said material is a woven fabric.

12. The improvement of claim 1 wherein said material is selected from the group consisting of water repellent resin-treated cotton fabric, resin-treated tight knitted cotton fabric and resin-treated rayon fabric.

13. The improvement of claim 1 wherein said material is impregnated with said compound and alkaline agent by padding the material, in an aqueous solution containing the compound and alkaline agent.

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UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 19, for "a continuation-in-part of" read -- related to --.

Signed and sealed this 29th day of August 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents